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ION BEAM GETTERING IN A^{III}—B^{V} COMPOUNDS COMPARED TO SILICON

By

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After a short survey on gettering problems in semiconductor technology new results concerning ion beam gettering for silicon and A^{III}—B^{V} compounds are reviewed.

Our own results in the field of ion beam gettering in GaP demonstrate that

(i) the gettering by implanted aluminium atoms is proved, and

(ii) the ion beam damage in GaP is suitable for the gettering of copper atoms.

1. Introduction

The term "gettering" comes from valve technology and denotes a technological step of vacuum improvement after sealing the tubes. In the field of semiconductor technology it was introduced by SHOCKLEY and GOETZBERGER [1].

The gettering process in semiconductors implies

(i) the binding of undesirable electrically active impurities and/or crystal defects into electrically inactive complexes;

(ii) the outdiffusion of metal atoms from space charge regions into surface layers and into interfaces;

(iii) the outdiffusion of dopants or the addition of atoms to bind undesirable electrically active atoms.

The first two kinds of gettering of mobile metal atoms in silicon include thermal annealing as well as gettering by phosphorous or boron silicate glass.

Estimating the impurity concentration of electrically active deep centres and the capture cross section to be $N_t \approx 5 \cdot 10^{13}\ \mathrm{cm}^{-3}$ and $\sigma \approx 5 \cdot 10^{-15}\ \mathrm{cm}^2$, respectively, for a p—n junction with an area of $A = 10^{-6}\ \mathrm{cm}^2$ and a space charge width of $W = (1$—$2)\ \mu\mathrm{m}$ one obtains for the generation current according to

$$I_{rg} = (qn_i\, AW)/2\,\tau, \tag{1}$$

a value of about 10^{-12} A.

According to

$$I_s = (qn_i\, sA_s)/2 \tag{2}$$

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the surface generation current will be of the same order of magnitude if the area of the space charge region at the surface and the surface recombination velocity are $A_s \approx 0.1$ A and $s \approx 10^3$ cm s^{-1}, respectively. For a camera tube in hybrid technology with about $5 \cdot 10^5$ to 10^6 diodes per chip, these values cause a total dark current of 500 to 1000 nA. Such a camera tube is suitable only in the case of a total dark current lower than 10 nA. That means that values of about 10 nA cm^{-2} and $5 \cdot 10^{-14}$ A for a single diode are required. These values are only obtained by phosphorous silicate glass gettering or by ion beam damage gettering [2 to 4]. Today, gettering processes including ion beam gettering [2, 4] are frequently used as steps in standard silicon technologies.

2. Gettering of deep centres in silicon

Backside gettering takes place during a thermal treatment in an inert gas atmosphere in consequence of a preceding damage process, which can be induced by mechanical treatment, ultrasonics, laser radiation or ion implantation. Sometimes the results are improved by a well-defined oxidation of the sample. In these cases oxygen is added to the inert gas.

The application of gettering processes leads to markedly higher yields in the production of integrated bipolar circuits as was shown by KEVASAN et al [5]. SAITOH et al [6] obtained a distinct improvement of the efficiency and of the I—U characteristics of polycrystalline solar cells by mechanical backside damage followed by a long-time thermal treatment (see Fig. 1). The gettering was found to be maximum at the surface and to be decreasing with depth.

The prolongation of the majority carrier lifetime by a factor up to 200 in case of laser radiation damage at the backside of the sample as shown by YANG and SCHWUTTKE [7] is an example for the high efficiency of gettering in particular cases.

Though the gettering process has not been completely explained until now, the migration is somewhat elucidated by the description of the process by an activation energy E_a derivable from the temperature- dependent concentration N_c of gettered atoms at the depth x for a constant time of thermal treatment according to

$$N_t = N_0 \exp\left\{-\frac{E_a}{kT}\right\} \exp\{\Theta t^{1/2}\}. \tag{3}$$

Here N_0 and Θ are constants. In this way SAH and WANG [8] derived an activation energy of $E_a = (2.15 \pm 0.05)$ eV from capacitance measurements for process-induced mid-gap centres. Gettering has been effected by phosphorous silicate glass with concentrations in the range from 10^{12} to 10^{13} cm^{-3}. By means

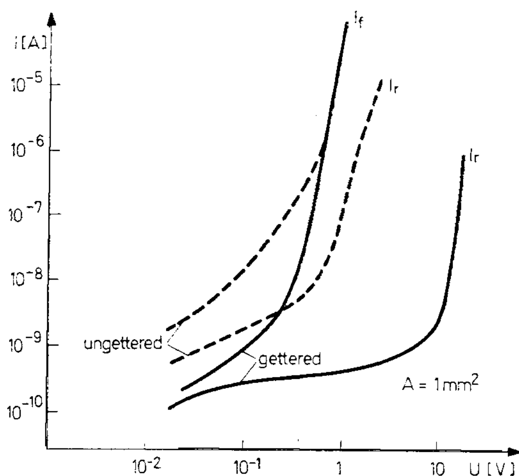

Fig. 1. Dark current characteristics of ungettered and gettered diodes (from [6])

of gettering the number of these process-induced centres may decrease to 10^{12} cm^{-3}. This low concentration facilitates the undisturbed operation of microelectronic silicon circuits as demonstrated above.

3. Ion beam gettering

Since the first publication in the field of ion beam gettering in 1972 [9] and the first application in 1973 [2] the new gettering method has developed into an effective technological procedure. The advantages of the ion beam getteiing compared to other methods are

(i) the high reproducibility of the damage conditions by the precise adjustment of dose, energy, temperature, and ion species;
(ii) the application of ions which become electrically inactive atoms inside the crystal;
(iii) the high-vacuum conditions of the process;
(iv) damage production through planar layers;
(v) gettering by the implanted ions themselves, and
(vi) lower annealing temperatures in comparison with glass gettering.

SEIDEL et al [10] were the first to carry out detailed research into the Si(Au) system by means of a Rutherford backscattering technique in connection with electron microscope investigations. The authors stated a higher efficiency of the ion beam gettering in the annealing temperature range below 1000 °C in comparison with the gettering by phosphorous glass and a comparable efficiency at an annealing temperature of 1150 °C. The ion beam gettering is used in the 1 μm — MOSFET technology to stabilize the lifetime of minority

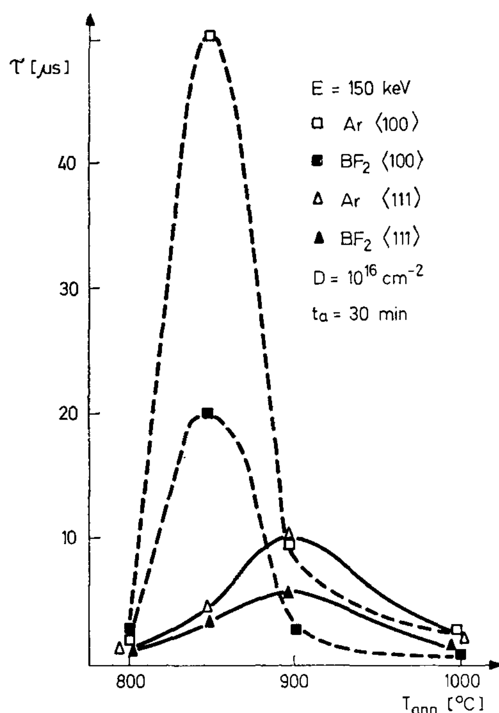

Fig. 2. Minority carrier lifetime in dependence on the annealing temperature T_{ann} for different gettering conditions (from [14])

carriers by a boron or argon ion backside implantation [11], for increasing the yields of bipolar circuits, for the diminution of dark currents, for increasing the minority carrier lifetime by a multiple argon ion backside implantation and annealing, and for the diminution of the density of the interface states of the SiO_2—Si system [13].

Measurements by Ryssel et al on argon damaged silicon show a strong dependence of gettering on ion species, crystal orientation, and temperature (Fig. 2) [14]. The measuring method was a phase shift technique in implanted p—n junctions of the same samples.

Bentini et al [15] described the high gettering efficiencies of gold in silicon at the comparatively low temperature of 500 °C (Fig. 3) [15]. This gettering with inert gettering atoms is very effective and demonstrates the applicability of ion beam gettering in silicon technology. Here the choice of the optimum gettering temperature is of particular importance to avoid the annealing of the damaged layer.

By means of oxygen implantation Favenec et al [16] presented the chromium gettering in the oxygen implantation profile in GaAs. This was probably the first ion beam gettering of that kind and the first recording of oxygen

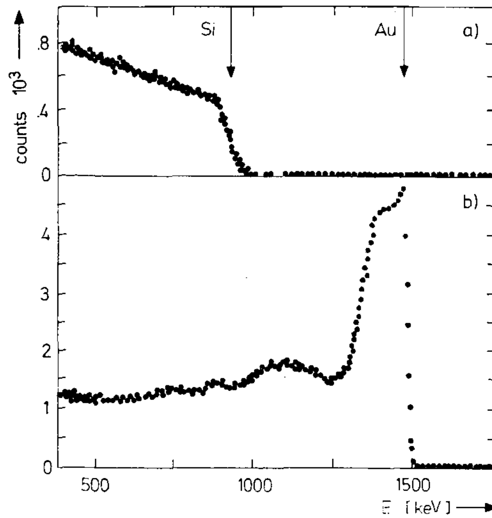

Fig. 3. Backscattering spectra for 1.6 MeV He^+ ions of the frontside from the undamaged (a) and damaged (b) backside regions of a silicon sample, showing the giant gettering effect for gold (from [15]) (gettering conditions: Ar^+, $E = 280$ keV, $D = 10^{16}$ cm^{-2}, $t_{ann} = 16$ h)

depth profiles. The gettering of chromium is highly important in GaAs electronics, because the redistribution of the chromium atoms takes already place at comparatively low annealing temperatures as it was shown by MAGEE et al [17]. Fig. 4 presents the results from these authors. According to Eq. (3) an activation energy of $E_a = (0.88 \pm 0.06)$ eV was derived.

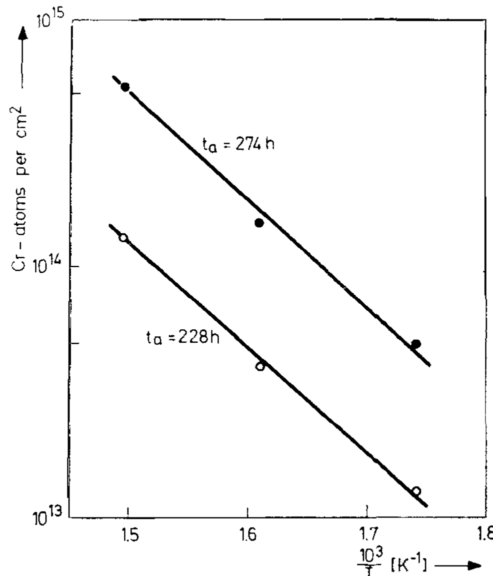

Fig. 4. Number of gettered Cr atoms in mechanically damaged surface layers of GaAs determined by SIMS for $t_{ann} = 274$ h (upper curve)and $t_{ann} = 228$ h (lower curve) (from [17])

As in the case of silicon technology, improved parameters should be expected by the application of ion beam gettering in the III—V technology, too. This suggestion is also supported by the results obtained for mechanically damaged GaAs(Au) and GaAs(Cr) [18 to 20]. The phosphorus glass gettering is a possible way in GaP as was shown by WESSELS [21].

4. Ion beam gettering in GaP

The efficiency of LED in GaP technology is limited by electrically active deep centres [22] which promote radiationless recombination, further by crystal defects [23], by the injection efficiency of incompletely optimized p—n structures [24], and by the influence of the surface [25, 26]. Here, gettering effects should be advantageous, especially the gettering by ion beam damage as explained above.

In many investigations of gettering effects secondary ion mass spectroscopy (SIMS) was used for the determination of gettered atom concentrations. The high detection sensitivity for a great number of elements, the mass resolution and the possibility of depth profiling are advantages, which recommend SIMS for the investigation of gettering processes. In the following investigations the secondary ion mass analyzer SMI 300 (CAMECA) was used. The depth calibrations were carried out by measuring the sputtering crater depths (Talystep, Taylor and Hobson). All ion implantations were performed by the special 350 kV accelerator of Humboldt University.

4.1. Aluminium implanted GaP

MÜRAU and BHARGAVA [27] have demonstrated the gettering of oxygen from lattice sites by aluminium atoms im LPE GaP and in LPE n—p structures, connected with an improvement of the green-to-red emission ratio. The diffusion length of the minority carriers is positively influenced by the aluminium atoms, too [27].

The influence of implanted aluminium atoms in VPE GaP and in diffused p—n structures of VPE GaP(N) has been investigated [28]. The investigations included measurements of the diffusion rate of the implanted aluminium atoms in GaP. By means of SIMS no diffusion was observed in bulk crystals (VPE layer on LEC wafer) up to annealing times of 60 minutes and temperatures up to 900 °C (Fig. 5). To prove the influence of the implanted aluminium atoms on the electro-optical parameters of the p—n junctions after annealing, it is necessary to use shallow p—n junctions or to use ions with energies in the MeV range, which correspond to projected ranges R_p of several microns.

By etching of p—n structures metallurgical depths of the p—n junctions of the same charge from 2.6 to 6 microns were obtained. Into these structures different doses of Al^{++} with $E = 600$ keV were implanted. Because of the technological process only an annealing at 510 °C for one hour in a hydrogen atmosphere was practicable.

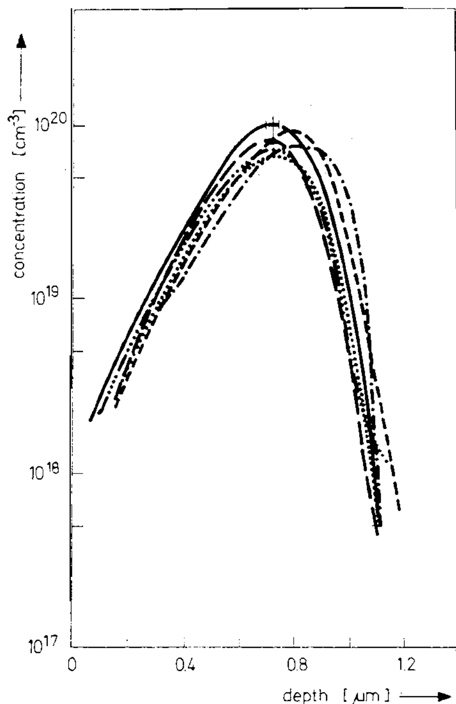

Fig. 5. SIMS depth profiles of Al^{++} implanted in GaP ($E = 600$ keV, $D = 2.7 \times 10^{15}$ cm^{-2}) ----- without annealing; ——— 600 °C, 1 h; —.—.—. 700 °C, 1 h; — — 800 °C, 1 h; ...... 850 °C, 15 min; —···— 900 °C, 30 min

The change in the injection luminescence of 3.8 μm deep p—n structures is demonstrated in Fig. 6. In Table I the data of the time constants are listed. From this investigation it can be concluded that

(i) the diffusion rate of aluminium in GaP is low;
(ii) the ion implantation of aluminium improves the ratio of the green-to-red emission in green LEDs;
(iii) gettering by the aluminium atoms influences the time constants of the minority carriers;
(iv) aluminium implantation changes the ratio of the emission from free to bound excitons.

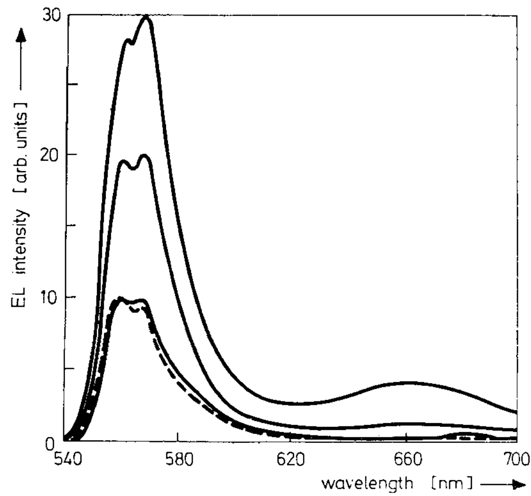

Fig. 6. Electroluminescence intensities in arbitrary units for a 3.8 μm deep *p-n* junction implanted with Al^{++} (600 keV), annealing temperature 510 °C, annealing time 1 h. Upper curve: without implantation, second curve: $D = 5 \times 10^{12}$ cm^{-2}, third curve $D = 5 \times 10^{13}$ cm^{-2}; dashed curve: $D = 5 \times 10^{14}$ cm^{-2}

These effects were distinctly marked although the implanted area covered was not more than one half of the *p—n* junction area and although the implanted aluminium atoms were spread within a layer thinner than 1 μm. Furthei investigations are required to enlighten whether the positive changes of the time constants aie caused by an improvement of the crystal quality owing to the gettering by the aluminium atoms, by the diminution of the surface recombination velocity owing to a formation of high-ohmic surface layers [26], or by a change of the injection ratio [29].

Table I

Time constants of Al^{++} implanted *p—n* junctions with a depth of 2,6 μm measured by recovery diode technique (τ_{rr}) and electroluminescence decay (τ_{el})

(E = 600 keV, T_{ann} = 510 °C, t_{ann} = 1 h)

D/cm^{-2}	τ_{el}/ns		τ_{rr}/ns with I_r = 20 mA		
	I_f = 20 mA	= 50 mA	= 100 mA	devices	wafer measurements
unimplanted	28	26	28	30	29 ± 9
5 · 10^{12}	60	46	50	34.5	37 ± 7
5 · 10^{13}	40	57	41	40	43 ± 3
5 · 10^{14}	39	61	55	39.5	42 ± 3

4.2. Gettering of copper in GaP VPE layers

The limitation of the lifetime of the minority carriers in the lower ns range may be influenced by copper or nickel impurities [30, 22]. Though the data available from the literature are different, two deep acceptor-like centres above the valence band with thermal activation energies of 0.51 eV and a

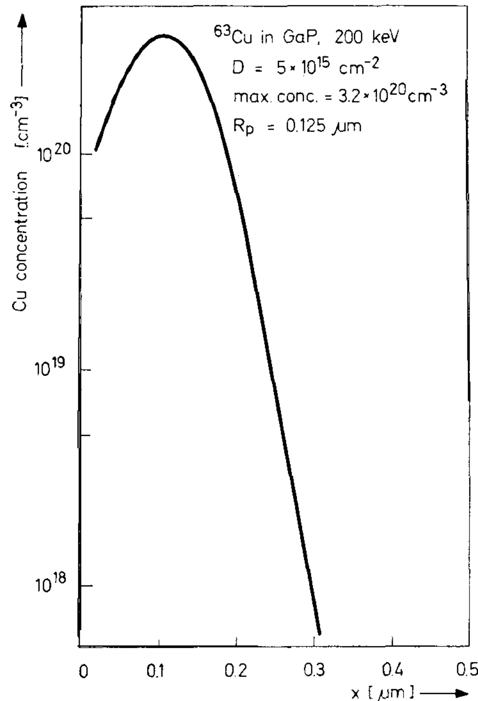

Fig. 7. SIMS depth profile of ^{63}Cu implanted in GaP ($D = 5 \times 10^{15}$ cm^{-2})

value in the range from 0.62 to 0.70 eV with cross sections of more than 10^{-16} cm^2 are certain [30 to 33]. Because of the high diffusion rate of copper in GaP, ion beam gettering seems to be able to diminish the copper concentration. Owing to this we performed investigations on the gettering of copper in GaP damaged by argon implantation and annealed by a subsequent procedure.

The investigations of the gettering of copper in the ion beam damage profiles were performed by SIMS. As no data are available for copper in GaP in the literature, the detection limit of this apparatus was tested by means of depth profiling of copper implantations. Into GaP VPE material various doses of ^{63}Cu of an energy of 200 keV were implanted in the range from 10^{14} cm^{-2} to $5 \cdot 10^{15}$ cm^{-2}. Fig. 7 shows a typical implantation profile. As primary ions positively charged oxygen of 5.5 keV energy was chosen. By reason of the

better signal-to-noise ratio it was not the $^{63}Cu^{+}$ signal but the $^{69}Ga^{63}Cu$ signal that has been recorded. From a great number of such data the detection limit for the measuring conditions described here was determined to be about $5 \cdot 10^{17}$ cm^{-3}, which certainly exceeds the value of the solubility of Cu in GaP, which has been estimated to be about $1 \cdot 10^{17}$ cm^{-3} at 950 °C and $2 \cdot 10^{16}$ cm^{-3} at 650 °C [34, 35]. To prove the possibility of the gettering of copper, the samples were prepared as follows: Argon with an energy of 300 keV and a dose of $2 \cdot 10^{15}$ cm^{-2} was implanted into the front of GaP VPE wafers. On the reverse side a copper layer of a thickness of 300 nm was vacuum-deposited

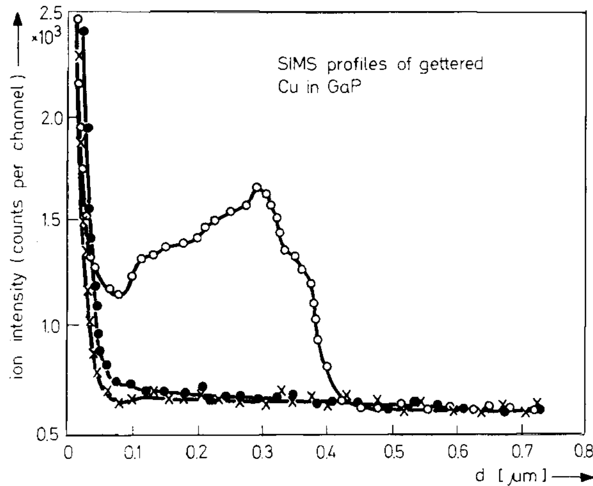

Fig. 8. SIMS depth profiles of copper in GaP (annealing temperature $T_{ann} = 500$ °C, $t_{ann} = 5$ h
○○○ sample copper deposited and argon damaged; ... sample copper deposited, undamaged
××× sample without damage and copper

The samples so prepared were annealed in a nitrogen atmosphere under different thermal conditions. Fig. 8 shows the depth profile of copper after a thermal treatment of 5 hours at 500 °C. From additional investigations using Rutherford backscattering (RBS) in these annealing conditions a sufficient damaged volume persists (95 to 98% damage, about 400 nm thick). From the Figure it can be deduced that copper decorates this damaged layer (curve 1). The depth profiles for a sample without copper (curve 2) and for a sample, which was only copper-deposited and annealed but not argon-implanted (curve 3), are indistinguishable, owing to the relatively low detection sensitivity compared to the solubility of copper of about 10^{17} cm^{-3}.

Fig. 9 exhibits the temperature dependence of this gettering effect. The concentration scale has been obtained from the procedure described above using implanted standard profiles. From the Figure it can be concluded that the gettering efficiency increases with increasing temperature. Simultaneously,

with increasing temperature the distribution of copper becomes more homogeneous in the damaged layer.

In the high temperature range a saturation effect of gettering seems to occur. To confirm this effect, further detailed investigations are necssary, especially in connection with the annealing of the damaged layer and distribution of high gettered copper concentration by means of SIMS and RBS measurements.

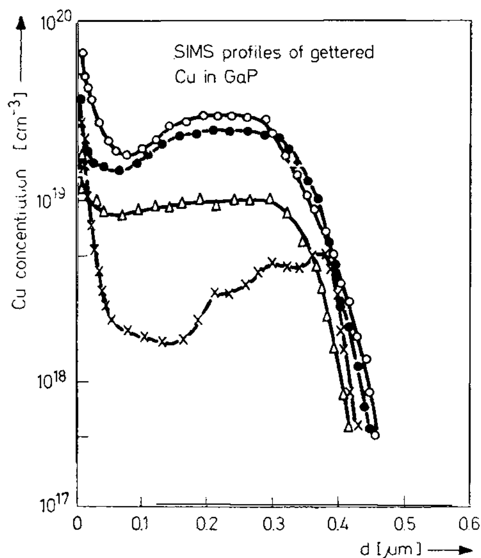

Fig. 9. SIMS depth profiles of copper in GaP showing the temperature dependence of ion beam gettering (× × × 600 °C, ▲▲▲ 650 °C, ... 700 °C, ○○○ 750 °C; t_{ann} = 1 h)

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